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METHOD FOR MANUFACTURING POLYMERIZED "NONMETALLOCENE" OLEFIN
POLYMERIZATION CATALYST

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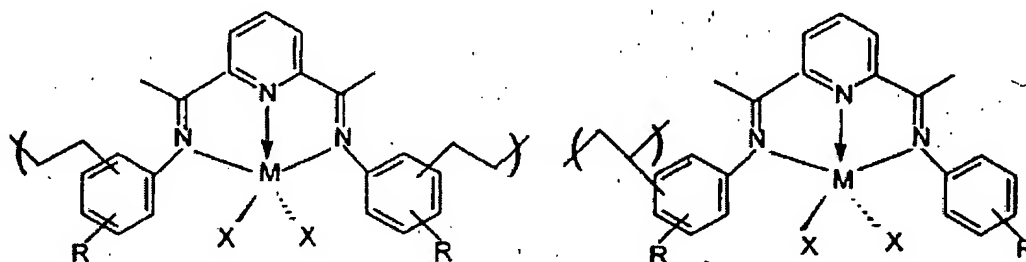
Abstract

The present invention pertains to the manufacture of a polymerized late transition metal "nonmetallocene" olefin polymerization catalyst. The catalyst consists of two components, that is components A and B. The chemical formula of component A is $[P(S\text{-}co\text{-}Cat)]$, wherein P represents a copolymer, S represents polystyrene, co represents copolymerization, and Cat represents a "nonmetallocene" catalyst. Cat is a coordination compound formed from a tridentate

nitrogen neutral ligand and a metal M. Component B is methylaluminoxane or boron pentachlorobenzene. These two types of catalysts have a relatively high catalytic activity when used for ethylene polymerization. The polymerization product contains no inorganic ash.

Claims

1. A method for manufacturing polymerized "nonmetallocene" olefin polymerization catalysts characterized by the following facts: the catalysts consist of two components, that is components A and B; the chemical formula of component A is $[P(S\text{-}co\text{-}Cat)]$, wherein P represents a copolymer, S represents polystyrene, co represents copolymerization, and Cat represents a "nonmetallocene" catalyst; the structure is as follows:

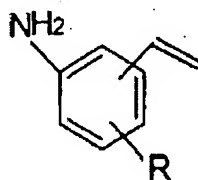


wherein, $M = Fe, Co$; $X = Cl, Br$; R is any type selected from H, Me, i-Pr, t-Bu; Cat is a coordination compound formed from a tridentate nitrogen neutral ligand and metal M; component B is methylaluminoxane or boron pentachlorobenzene;

the catalyst is manufactured as follows:

1) preparation of an alkylene arylamine

the structure is as follows:



under oxygen-free and anhydrous conditions, with 50-70 mL of tetrahydrofuran used as the solvent, under cooling of ice water, 51-74 mmol of methyltriphenylphosphorous bromide is added to react with 51-78 mmol of n-butyllithium; after 30-60 min, 50-74 mmol of a nitroarylaldehyde are added, and the reaction is carried out for 12-18 h; the obtained mixed solution is washed with brine, followed by extraction using trichloromethane; after drying with anhydrous sodium sulfate, the extract is concentrated in vacuo; the remaining solution is passed through a silica gel column for separation with 1:1 toluene/hexane used as the rinsing agent; as a result, a nitroarylethylene is obtained at a yield of 72-89%; then, the product is reduced through an iron - acetic acid - alcohol system to obtain an alkylene arylamine at a yield of 56-60%;

2) preparation of symmetric tridentate ligand containing two alkylene groups

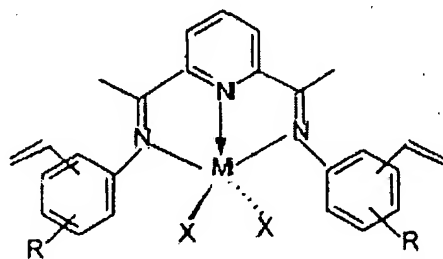
with 20-30 mL of methanol used as the solvent, 1-2 mL of glacial acetic acid, 0.94-1.5 mL of an alkylene arylamine, and 3.05-4.9 mmol of 2,6-diacetylpyridine are heated to slightly boiling under the protection of argon, followed by 4 h of reflux and concentration in vacuo; then, the reaction product is added to 30 mL of deionized water and extracted using ethyl ether; the extract is dried with anhydrous sodium sulfate and concentrated; the system is cooled for crystallization to obtain a diimino ligand as yellow crystals at a yield of 80-85%;

3) preparation of asymmetric tridentate ligand containing one alkylene group

with 20-30 mL of anhydrous alcohol used as the solvent and 0.5-1 mL of glacial acetic acid used as the catalyst, 0.8-1.5 mL of an alkylene arylamine is reacted with 6.1-11.4 mmol of 2,6-diacetylpyridine under stirring at room temperature for 3-4 days; the solution is light yellow in color; after the solvent is removed, 30-40 mL of deionized water are added; a yellow precipitate appears and is filtered; the precipitate is recrystallized using n-hexane to obtain a monoimino compound; 3.8-5.0 mmol of the obtained monoimino compound, 8.3-10.9 mmol of an arylamine, and 1-2 mL of glacial acetic acid are added to 20-30 mL of methanol, followed by 2-3 h of reflux performed under the protection of argon; after the solvent is removed, the system is cooled for crystallization, giving an asymmetric diimino ligand at a yield of 53-65%;

4) preparation of symmetric late transition metal catalyst containing two alkylene groups

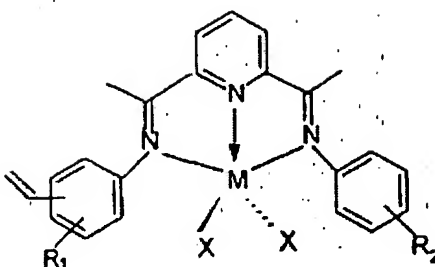
the structure is as follows:



the catalyst is prepared under oxygen-free and anhydrous conditions and under the protection of highly pure argon; with 30-40 mL of tetrahydrofuran used as the solvent, the symmetric diimino ligand and iron dichloride tetrahydrate or anhydrous cobalt dichloride are added at an amount ratio of 1:1:1 and stirred at room temperature for 1-2 h, followed by concentration in vacuo; n-hexane is added to precipitate a solid powder, which is washed 3-5 times with n-hexane, followed by drying in vacuo; the yield is 95-98%;

5) preparation of asymmetric late transition metal catalyst containing one alkylene group

the structure is as follows:



the catalyst is prepared under oxygen-free and anhydrous conditions and under the protection of highly pure argon; with 30-40 mL of tetrahydrofuran used as the solvent, the asymmetric ligand and iron dichloride tetrahydrate or anhydrous cobalt dichloride are added at an amount ratio of 1.05:1 and stirred at room temperature for 1.5-3 h, followed by concentration in vacuo; n-hexane is added to precipitate a solid powder, which is washed 3-5 times with n-hexane, followed by drying in vacuo; the yield is 92-96%;

6) preparation of polymerized “nonmetallocene” catalyst

under oxygen-free and anhydrous conditions, 2-10 mmol of the alkylene-containing “nonmetallocene” catalyst, 5-10 mL of styrene and 0.05-0.14 g of azodiisobutyronitrile are added sequentially to boiling dimethylamide, where they are mixed homogeneously; then, copolymerization is carried out in an 80°C water bath for 12-15 h; after that, the dimethylamide is removed under heat to obtain a gel-like substance, which is dissolved using 30 mL of toluene, followed by centrifugation; the supernatant is treated with n-hexane used as a precipitating agent to obtain a solid powder, which is washed with n-hexane three times, followed by drying; ethylene polymerization is carried out under oxygen-free and anhydrous conditions; 100 mL of toluene or hexane, methylaluminoxane, polymerized catalyst Al/M=500-2500 and ethylene are added sequentially to the reaction system; the reaction is carried out at 25-50°C for 1 h; a methanol solution containing 1% hydrochloric acid is used to end the reaction; the obtained product is filtered and washed with methanol three times, followed by drying in vacuo at 40°C for 24 h.

2. The method for manufacturing polymerized “nonmetallocene” olefin polymerization catalysts described in Claim 1 characterized by the fact that the symmetric diimino ligand and iron dichloride tetrahydrate are added at a ratio of 1.1:1.

3. The method for manufacturing polymerized “nonmetallocene” olefin polymerization catalysts described in Claim 1 characterized by the fact that the the symmetric diimino ligand and anhydrous cobalt dichloride are added at a ratio of 1.1:1.

4. The method for manufacturing polymerized “nonmetallocene” olefin polymerization catalysts described in Claim 1 characterized by the fact the asymmetric diimino ligand and iron dichloride tetrahydrate are added at a ratio of 1.05:1.

5. The method for manufacturing polymerized "nonmetallocene" olefin polymerization catalysts described in Claim 1 characterized by the fact that the asymmetric diimino ligand and anhydrous cobalt dichloride are added at a ratio of 1.05:1.

6. The method for manufacturing polymerized "nonmetallocene" olefin polymerization catalysts described in Claim 1 characterized by the fact that the aforementioned ethylene polymerization is carried out under oxygen-free and anhydrous conditions, and 100 mL of toluene are added to the reaction system.

7. The method for manufacturing polymerized "nonmetallocene" olefin polymerization catalysts described in Claim 1 characterized by the fact that the aforementioned ethylene polymerization is carried out under oxygen-free and anhydrous conditions, and 100 mL of hexane are added to the reaction system.

8. The method for manufacturing polymerized "nonmetallocene" olefin polymerization catalysts described in Claim 1 characterized by the fact that the aforementioned ethylene polymerization is carried out under oxygen-free and anhydrous conditions and methylaluminoxane and polymerized catalyst Al/M=500-2500 are added to the reaction system.

9. The method for manufacturing polymerized "nonmetallocene" olefin polymerization catalysts described in Claim 1 characterized by the fact that the aforementioned ethylene polymerization is carried out under oxygen-free and anhydrous conditions, and ethylene is added to the reaction system.

Specification

The present invention pertains to a method for manufacturing polymerized "nonmetallocene" late transition metal olefin polymerization catalysts.

Polyolefin is a prominent material in the modern polymer materials industry. Millions of tons of polyolefin products are manufactured annually. These products improve the quality of life of people. Under the effect of catalysts, olefins are polymerized to generate polymers. Polyolefin products with special structures and properties can be obtained by varying the structure of the catalysts. Therefore, the catalyst is the key to the polyolefin industry. In recent years, a series of new olefin polymerization catalysts with one active center have been discovered that are based on metallocene catalysts. This series of catalysts can be roughly classified into two types: a. nonmetallocene compounds and non-group IVB transition metal compounds; b. polyimino compounds of late transition metals, such as nickel, palladium, iron, cobalt, etc. Since this series of catalysts were discovered after the metallocene catalysts, they are generally called "nonmetallocene" olefin polymerization catalysts.

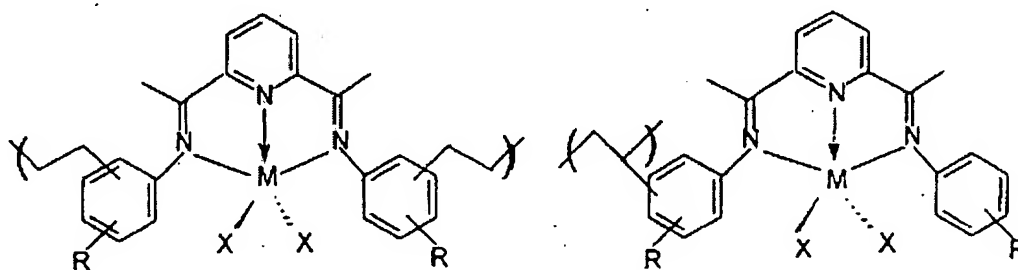
In 1998, Brookhart, et al. and the Du Pont Co. (J. Am. Chem. Soc. 120. 4049 (1998), WO98/30612, WO98/27214) and Gibson, et al. and the BP Co. (Chem. Commun. 849. 1998,

WO99/12981) reported that polyimino compounds of iron and cobalt are able to catalyze olefin polymerization in the presence of an auxiliary catalyst MMAO and show very high activity. This discovery opened a new field of research of "nonmetallocene" olefin polymerization catalysts. When the polyiminio compound of iron or cobalt is used to catalyze ethylene polymerization to generate linear high-density polyethylene, the molecular weight of the polymer is easily affected by substituents, the central metal atom, and the concentration of the active points. The Brookhart group and the Gibson group studied the influences of the substituents at positions 2, 4, 6 in arylamines on the structure and catalytic property of the catalyst. The substituents included methyl, isopropyl, and tert-butyl groups. From the research it was found that larger substituents at positions 2, 6 tend to generate polyethylene with a high molecular weight. So far, there has been no report on carrying late transition metal "nonmetallocene" catalysts on solid carriers. A solid carrier is significant in terms of making this type of catalyst suitable for industrial apparatuses.

The purpose of the present invention is to provide a method for manufacturing polymerized "nonmetallocene" olefin polymerization catalysts. This method uses an alkylene containing a polyimino compound of iron or cobalt and styrene to couple a "nonmetallocene" catalyst to a polymer chain via the σ chain under the effect of an initiator to form a polymerized "nonmetallocene" olefin polymerization catalyst.

The polymerized "nonmetallocene" catalyst also has very high catalytic activity in olefin polymerization. In addition, when the "nonmetallocene" catalyst is polymerized, it becomes very easy to control the composition and distribution of the catalyst on the polymer chain. The catalytic effect of the active center can be fully displayed by adjusting the distribution of the catalyst on the polymer chain. Also, the polymer obtained by using the polymerized "nonmetallocene" catalyst to catalyze the olefin polymerization contains no ash component.

The catalyst of the present invention consists of two components, that is components A and B. The chemical formula of component A is $[P(S\text{-}co\text{-}Cat)]$, wherein P represents a copolymer, S represents polystyrene, co represents copolymerization, and Cat represents a "nonmetallocene" catalyst. The structure is as follows:

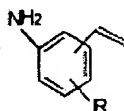


wherein, M=Fe, Co; X=Cl, Br; R is any type selected from H, Me, I-Pr, t-Bu. Cat is a coordination compound formed from a tridentate nitrogen neutral ligand and a metal M. Through copolymerization with styrene, the alkylene groups at the ortho, meta, para positions in the amine can couple the catalyst to a polymer chain via the σ chain to obtain the polymerized "nonmetallocene" olefin polymerization catalyst. Component B is methylaluminoxane or boron pentachlorobenzene.

The catalyst is manufactured as follows:

1) Preparation of alkylene arylamine

The structure is as follows:



Under oxygen-free and anhydrous conditions, with 50-70 mL of tetrahydrofuran used as the solvent, under cooling of ice water, 51-74 mmol of methyltriphenylphosphorous bromide is added to react with 51-78 mmol of n-butyllithium. After 30-60 min, 50-74 mmol of nitroarylaldehyde is added, and the reaction is carried out for 12-18 h. The obtained mixed solution is washed with brine, followed by extraction using trichloromethane. After drying with anhydrous sodium sulfate, the extract is concentrated in vacuo; the remaining solution is passed through a silica gel column for separation with 1:1 toluene/hexane used as the rinsing agent. As a result, a nitroarylethylene is obtained at a yield of 72-89%. Then, the product is reduced through an iron – acetic acid – alcohol system to obtain an alkylene arylamine at a yield of 56-60%.

2) Preparation of symmetric tridentate ligand containing two alkylene groups

With 20-30 mL of methanol used as the solvent, 1-2 mL of glacial acetic acid, 0.94-1.5 mL of an alkylene arylamine, and 3.05-4.9 mmol of 2,6-diacetylpyridine are heated to slightly boiling under the protection of argon, followed by 4 h of reflux and concentration in vacuo. Then, the reaction product is added to 30 mL of deionized water and extracted using ethyl ether. The extract is dried with anhydrous sodium sulfate and concentrated. The system is cooled for crystallization to obtain a diimino ligand as yellow crystals at a yield of 80-85%.

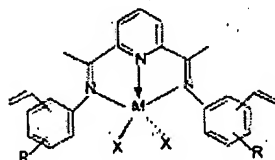
3) Preparation of asymmetric tridentate ligand containing one alkylene group

With 20-30 mL of anhydrous alcohol used as the solvent and 0.5-1 mL of glacial acetic acid used as the catalyst, 0.8-1.5 mL of an alkylene arylamine is reacted with 6.1-11.4 mmol of 2,6-diacetylpyridine under stirring at room temperature for 3-4 days. The solution is light yellow in color. After the solvent is removed, 30-40 mL of deionized water are added. A yellow precipitate appears and is filtered. The precipitate is recrystallized using n-hexane to obtain a

monoimino compound. 3.8-5.0 mmol of the obtained monoimino compound, 8.3-10.9 mmol of an arylamine, and 1-2 mL of glacial acetic acid are added to 20-30 mL of methanol, followed by 2-3 h of reflux performed under the protection of argon. After the solvent is removed, the system is cooled for crystallization, giving an asymmetric diimino ligand at a yield of 53-65%.

4) Preparation of symmetric late transition metal catalyst containing two alkylene groups

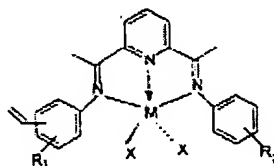
The structure is as follows:



The catalyst is prepared under oxygen-free and anhydrous conditions and under protection of highly pure argon. With 30-40 mL of tetrahydrofuran used as the solvent, the symmetric diimino ligand and iron dichloride tetrahydrate or anhydrous cobalt dichloride are added in an amount ratio of 1:1:1 and stirred at room temperature for 1-2 h, followed by concentration in vacuo; n-hexane is added to precipitate a solid powder, which is washed 3-5 times with n-hexane, followed by drying in vacuo. The yield is 95-98%.

5) Preparation of asymmetric late transition metal catalyst containing one alkylene group

The structure is as follows:



The catalyst is prepared under oxygen-free and anhydrous conditions and under protection of highly pure argon. With 30-40 mL of tetrahydrofuran used as the solvent, the asymmetric ligand and iron dichloride tetrahydrate or anhydrous cobalt dichloride are added in an amount ratio of 1.05:1 and stirred at room temperature for 1.5-3 h, followed by concentration in vacuo; n-hexane is added to precipitate a solid powder, which is washed 3-5 times with n-hexane, followed by drying in vacuo. The yield is 92-96%.

6) Preparation of polymerized “nonmetallocene” catalyst

Under oxygen-free and anhydrous conditions, 2-10 mmol of the alkylene-containing “nonmetallocene” catalyst, 5-10 mL of styrene, 0.05-0.14 g of azodiisobutyronitrile are added sequentially to boiling dimethylamide, where they are mixed homogeneously. Then, copolymerization is carried out in an 80°C water bath for 12-15 h. After that, the dimethylamide

is removed as much as possible under heating to obtain a gel-like substance, which is dissolved using 30 mL of toluene, followed by centrifugation. The supernatant is treated with n-hexane used as a precipitating agent to obtain a solid powder, which is washed with n-hexane three times, followed by drying.

Ethylene polymerization is carried out under oxygen-free and anhydrous conditions. 100 mL of toluene or hexane, methylaluminoxane, polymerized catalyst Al/M=500-2500 and ethylene are added sequentially to the reaction system. The reaction is carried out at 25-50°C for 1 h. A methanol solution containing 1% hydrochloric acid is used to end the reaction. The obtained product is filtered and washed with methanol three times, followed by drying in vacuo at 40°C for 24 h.

The application examples of the present invention are as follows.

Application Example 1: Preparation of alkylene arylamine

In an argon atmosphere, 51 mmol of methyltriphenylphosphorous bromide were dissolved in 50 mL of dry tetrahydrofuran. Under cooling of ice water, 32 mL of 1.6M n-butyllithium are added to the solution. After 30 min, 100 mL of a tetrahydrofuran solution containing 50 mmol of o-nitrobenzaldehyde were added, and the reaction was carried out for 12 h. The obtained mixed solution was washed with brine, followed by extraction using trichloromethane. After drying with anhydrous sodium sulfate, the extract was concentrated in vacuo. The remaining solution was passed through a silica gel column for separation with toluene/hexane 1:1 used as the rinsing agent. As a result, 6.63 g of a yellow liquid, o-nitrostyrene, was obtained at a yield of 89.0%. 45 mmol of the obtained n-nitrostyrene were dissolved in a mixed solution consisting of 50 mL of glacial acetic acid and 50 mL of anhydrous alcohol, followed by adding 0.178 mmol of iron powder. The mixed solution was refluxed under the protection of argon for 1h. After the system was cooled to room temperature, the reaction product was added to 350 mL of water and neutralized with solid sodium carbonate. The condensed solution was extracted with ether, followed by concentration in vacuo. A small amount of benzenediol was added to the remaining solution, followed by distillation under reduced pressure, giving 3.2 g of a colorless liquid, o-aminostyrene, at a yield of 60.0%.

Application Example 2: Preparation of alkylene arylamine

The process was carried out in the same way as described in Application Example 1 except that m-nitrobenzaldehyde was used in an amount of 50 mmol, and 2.17 g of m-aminostyrene were obtained at a yield of 41.5%.

Application Example 3: Preparation of alkylene arylamine

The process was carried out in the same way as described in Application Example 1 except that p-nitrobenzaldehyde was used in an amount of 50 mmol, and 3.02 g of p-aminostyrene were obtained at a yield of 50.7%.

Application Example 4: Preparation of alkylene arylamine

In an argon atmosphere, 74 mmol of methyltriphenylphosphorous bromide was dissolved in 70 mL of dry tetrahydrofuran. Under cooling of ice water, 48.8 mL of 1.6M n-butyllithium are added to the solution. After 50 min, 100 mL of a tetrahydrofuran solution containing 74 mmol of 3-nitro-4-methylbenzaldehyde were added, and the reaction was carried out for 16 h under stirring. The obtained mixed solution was washed with brine, followed by extraction using trichloromethane. After drying with anhydrous sodium sulfate, the extract was concentrated in vacuo. The remaining solution was passed through a silica gel column for separation with 1:1 toluene/hexane used as the rinsing agent. As a result, 8.68 g of a yellow liquid, 3-nitro-4-methylstyrene, were obtained at a yield of 72.0%. 45 mmol of the obtained n-nitrostyrene [sic] were dissolved in a mixed solution consisting of 50 mL of glacial acetic acid and 50 mL of anhydrous alcohol, followed by adding 0.178 mmol of iron powder. The mixed solution was refluxed under the protection of argon for 1 h. After the system was cooled to room temperature, the reaction product was added to 350 mL of water and neutralized with solid sodium carbonate. The condensed solution was extracted with ether, followed by concentration in vacuo. A small amount of benzenediol was added to the remaining solution, followed by distillation under reduced pressure, giving 3.41 g of a colorless liquid, 3-amino-4-methylstyrene, at a yield of 57%.

Application Example 5: Preparation of alkylene arylamine

In an argon atmosphere, 60 mmol of methyltriphenylphosphorous bromide was dissolved in 60 mL of dry tetrahydrofuran. Under cooling of ice water, 37.5 mL of 1.6M n-butyllithium are added to the solution. After 60 min, 100 mL of a tetrahydrofuran solution containing 60 mmol of 3-isopropyl-4-nitrobenzaldehyde was added, and the reaction was carried out for 18 h under stirring. The obtained mixed solution was washed with brine, followed by extraction using trichloromethane. After drying with anhydrous sodium sulfate, the extract was concentrated in vacuo. The remaining solution was passed through a silica gel column for separation with 1:1 toluene/hexane used as the rinsing agent. As a result, 9.11 g of a yellow liquid, 3-isopropyl-4-nitrostyrene, was obtained at a yield of 79.5%. 45 mmol of the obtained n-nitrostyrene [sic] were dissolved in a mixed solution consisting of 50 mL of glacial acetic acid and 50 mL of anhydrous alcohol, followed by adding 0.178 mmol of iron powder. The mixed

solution was refluxed under the protection of argon for 1 h. After the system was cooled to room temperature, the reaction product was added to 350 mL of water and neutralized with solid sodium carbonate. The condensed solution was extracted with ether, followed by concentration in vacuo. A small amount of benzenediol was added to the remaining solution, followed by distillation under reduced pressure, giving 4.06 g of a colorless liquid, 3-isopropyl-4-nitrostyrene, at a yield of 56.0%.

Application Example 6: Preparation of asymmetric tridentate ligand containing one alkylene group

With 20 mL of anhydrous alcohol used as the solvent and 0.5 mL of glacial acetic acid used as the catalyst, 0.8 mL of o-aminostyrene was reacted with 6.1 mmol of 2,6-diacetylpyridine under stirring at room temperature for 3 days. The solution was light yellow in color. After most of the solvent was removed, 30 mL of deionized water were added. A yellow precipitate appeared and was filtered. The precipitate was recrystallized using n-hexane to obtain a monoimino compound of columnar crystals. 3.8 mmol of the obtained monoimino compound, 8.3 mmol of 2,6-dimethylaniline, and 1 mL of glacial acetic acid were added to 20 mL of methanol, followed by 2 h of reflux performed under protection of argon. After part of the solvent was removed, the system was cooled for crystallization, giving 0.91 g of an asymmetric diimino ligand o-C₂₅H₂₅N₃, at a yield of 65%.

Application Example 7: Preparation of asymmetric tridentate ligand containing one alkylene group

With 30 mL of anhydrous alcohol used as the solvent and 1 mL of glacial acetic acid used as the catalyst, 1.2 mL of 3-amino-4-methylstyrene were reacted with 8.5 mmol of 2,6-diacetylpyridine under stirring at room temperature for 4 days. The solution was light yellow in color. After most of the solvent was removed, 40 mL of deionized water were added. A yellow precipitate appeared and was filtered. The precipitate was recrystallized using n-hexane to obtain a monoimino compound of columnar crystals. 4.0 mmol of the obtained monoimino compound, 10.0 mmol of 2,6-dimethylaniline, and 1 mL of glacial acetic acid were added to 25 mL of methanol, followed by 3 h of reflux performed under protection of argon. After part of the solvent was removed, the system was cooled for crystallization, giving 0.88 g of an asymmetric diimino ligand, o-C₂₆H₂₇N₃, at a yield of 58%.

Application Example 8: Preparation of asymmetric tridentate ligand containing one alkylene group

With 30 mL of anhydrous alcohol used as the solvent and 1 mL of glacial acetic acid used as the catalyst, 1.5 mL of 3-isopropyl-4-aminostyrene were reacted with 1.4 mmol of 2,6-diacetylpyridine under stirring at room temperature for 4 days. The solution was light yellow in color. After most of the solvent was removed, 40 mL of deionized water were added. A yellow precipitate appeared and was filtered. The precipitate was recrystallized using n-hexane to obtain a monoimino compound of columnar crystals. 5.0 mmol of the obtained monoimino compound, 10.9 mmol of 2,6-diisopropylaniline, and 2 mL of glacial acetic acid were added to 30 mL of methanol, followed by 2.5 h of reflux performed under protection of argon. After part of the solvent was removed, the system was cooled for crystallization, giving 1.23 g of an asymmetric diimino ligand, o-C₃₂H₃₉N₃, at a yield of 53%.

Application Example 9: Preparation of symmetric tridentate ligand containing two alkylene groups

With 20 mL of methanol used as the solvent, 1 mL of glacial acetic acid, 0.94 mL of o-aminostyrene, and 3.05 mmol of 2,6-diacetylpyridine were heated to slightly boiling under protection of argon, followed by 4 h of reflux and concentration in vacuo. Then, the reaction product was added to 30 mL of deionized water and extracted using ethyl ether. The extract was dried with anhydrous sodium sulfate and concentrated. The system was cooled for crystallization to obtain 0.95 g of a yellow crystal of a diimino ligand, o,o-C₂₅H₂₃N₃, at a yield of 85%.

Application Example 10: Preparation of symmetric tridentate ligand containing two alkylene groups

With 20 mL of methanol used as the solvent, 2 mL of glacial acetic acid, 1.2 mL of m-aminostyrene, and 3.92 mmol of 2,6-diacetylpyridine were added at the same time. The process was carried out in the same way as described in Application Example 9, giving 1.17 g of a diimino ligand, m,m-C₂₅H₂₃N₃, at a yield of 82%.

Application Example 11: Preparation of symmetric tridentate ligand containing two alkylene groups

With 30 mL of methanol used as the solvent, 2 mL of glacial acetic acid, 1.5 mL of p-aminostyrene, and 4.9 mmol of 2,6-diacetylpyridine were added at the same time. The process was carried out in the same way as described in Application Example 9, giving 1.43 g of a diimino ligand, p,p-C₂₅H₂₃N₃, at a yield of 80%.

Application Example 12: Preparation of late transition metal compound containing one alkylene group

Under oxygen-free and anhydrous conditions and under the protection of highly pure argon, 1.51 mmol of the ligand $o\text{-C}_{25}\text{H}_{25}\text{N}_3$ obtained in Application Example 6 were added to 30 mL of tetrahydrofuran, followed by adding 1.44 mmol of iron dichloride tetrahydrate. The system was stirred at room temperature for 1.5 h, followed by concentration in vacuo. n-hexane was added to precipitate a solid powder, which was washed 3 times with n-hexane, followed by drying in vacuo, giving 0.682 g of $o\text{-C}_{25}\text{H}_{25}\text{N}_3\text{Fe}$ at a yield of 96%.

Application Example 13: Preparation of late transition metal compound containing one alkylene group

Under oxygen-free and anhydrous conditions and under the protection of highly pure argon, 1.51 mmol of the ligand $o\text{-C}_{26}\text{H}_{27}\text{N}_3$ obtained in Application Example 7 was added to 35 mL of tetrahydrofuran, followed by adding 1.44 mmol of iron dichloride tetrahydrate. The system was stirred at room temperature for 2 h, followed by concentration in vacuo. n-hexane was added to precipitate a solid powder, which was washed 3 times with n-hexane, followed by drying in vacuo, giving 0.695 g of $o\text{-C}_{26}\text{H}_{27}\text{N}_3\text{Fe}$ at a yield of 95%.

Application Example 14: Preparation of late transition metal compound containing one alkylene group

Under oxygen-free and anhydrous conditions and under the protection of highly pure argon, 1.51 mmol of the ligand $o\text{-C}_{32}\text{H}_{39}\text{N}_3$ obtained in Application Example 8 was added to 30 mL of tetrahydrofuran, followed by adding 1.44 mmol of anhydrous cobalt dichloride. The system was stirred at room temperature for 1.5 h, followed by concentration in vacuo. n-hexane was added to precipitate a solid powder, which was washed 5 times with n-hexane, followed by drying in vacuo, giving 0.788 g of $o\text{-C}_{32}\text{H}_{39}\text{N}_3\text{Co}$ at a yield of 92%.

Application Example 15: Preparation of late transition metal compound containing one alkylene group

Under oxygen-free and anhydrous conditions and under the protection of highly pure argon, 1.51 mmol of the ligand $o,o\text{-C}_{25}\text{H}_{23}\text{N}_3$ obtained in Application Example 9 was added to 30 mL of tetrahydrofuran, followed by adding 1.37 mmol of iron dichloride tetrahydrate. The system was stirred at room temperature for 1.5 h, followed by concentration in vacuo. n-hexane was added to precipitate a solid powder, which was washed 4 times with n-hexane, followed by drying in vacuo, giving 0.64 g of $o,o\text{-C}_{25}\text{H}_{23}\text{N}_3\text{Fe}$ at a yield of 95%.

Application Example 16: Preparation of late transition metal compound containing one alkylene group

Under oxygen-free and anhydrous conditions and under protection of highly pure argon, 1.51 mmol of the ligand $m,m\text{-C}_{25}\text{H}_{23}\text{N}_3$ obtained in Application Example 10 was added to 30 mL of tetrahydrofuran, followed by adding 1.37 mmol of iron dichloride tetrahydrate. The system was stirred at room temperature for 1 h, followed by concentration in vacuo. n-hexane was added to precipitate a solid powder, which was washed 5 times with n-hexane, followed by drying in vacuo, giving 0.647 g of $m,m\text{-C}_{25}\text{H}_{23}\text{N}_3\text{Fe}$ at a yield of 96%.

Application Example 17: Preparation of late transition metal compound containing one alkylene group

Under oxygen-free and anhydrous conditions and under protection of highly pure argon, 1.51 mmol of the ligand $p,p\text{-C}_{32}\text{H}_{23}\text{N}_3$ obtained in Application Example 11 was added to 30 mL of tetrahydrofuran, followed by adding 1.37 mmol of anhydrous cobalt dichloride. The system was stirred at room temperature for 2 h, followed by concentration in vacuo. n-hexane was added to precipitate a solid powder, which was washed 3 times with n-hexane, followed by drying in vacuo, giving 0.664 g of $o\text{-C}_{25}\text{H}_{23}\text{N}_3\text{Co}$ at a yield of 98%.

Application Example 18: Preparation of catalyst component A

Under anhydrous conditions, 2.0 mmol of the alkylene-containing catalyst $o\text{-C}_{25}\text{H}_{23}\text{N}_3\text{Fe}$ obtained in Application Example 12 was added to 20 mL boiling dimethylamide, followed by adding 5 mL of styrene and 0.05 g of azodiisobutyronitrile. The reaction was carried out in an 80°C water bath for 12 h. Then, the dimethylamide was removed as much as possible under heating to obtain a gel-like substance, which was dissolved using 30 mL of toluene, followed by centrifugation. The supernatant was treated with n-hexane to obtain a solid powder, which was washed with n-hexane three times, giving catalyst component A $p[\text{S-co-(}o\text{-C}_{25}\text{H}_{23}\text{N}_3\text{Fe)}]$. The measured Fe content was 0.6 wt%.

Application Example 19: Preparation of catalyst component A

Under anhydrous conditions, 5.0 mmol of the alkylene containing catalyst $o,o\text{-C}_{25}\text{H}_{23}\text{N}_3\text{Fe}$ obtained in Application Example 15 was added to 20 mL boiling dimethylamide, followed by adding 8 mL of styrene and 0.1 g of azodiisobutyronitrile. The reaction was carried out in an 80°C water bath for 14 h. Then, the dimethylamide was removed as much as possible under heating to obtain a gel-like substance, which was dissolved using 30 mL of toluene, followed by centrifugation. The supernatant was treated with n-hexane to

obtain a solid powder, which was washed with n-hexane three times, giving catalyst component A p[S-co-(o,o-C₂₅H₂₃N₃Fe)]. The measured Fe content was 1.46 wt%.

Application Example 20: Preparation of catalyst component A

Under anhydrous conditions, 10 mmol of the alkylene containing catalyst m,m-C₂₅H₂₃N₃Fe obtained in Application Example 16 was added to 20 mol boiling dimethylamide, followed by adding 10 mL of styrene and 0.14 g of azodiisobutyronitrile. The reaction was carried out in an 80°C water bath for 15 h. Then, the dimethylamide was removed as much as possible under heating to obtain a gel-like substance, which was dissolved using 30 mL of toluene, followed by centrifugation. The supernatant was treated with n-hexane to obtain a solid powder, which was washed with n-hexane three times, giving catalyst component A p[S-co-(m,m-C₂₅H₂₃N₃Fe)]. The measured Fe content was 0.7 wt%.

Application Example 21: Preparation of catalyst component A

Under anhydrous conditions, 10 mmol of the alkylene containing catalyst p,p-C₂₅H₂₃N₃Co obtained in Application Example 17 was added to 20 mol boiling dimethylamide, followed by adding 10 mL of styrene and 0.14 g of azodiisobutyronitrile. The reaction was carried out in an 80°C water bath for 15 h. Then, the dimethylamide was removed as much as possible under heating to obtain a gel-like substance, which was dissolved using 30 mL of toluene, followed by centrifugation. The supernatant was treated with n-hexane to obtain a solid powder, which was washed with n-hexane three times, giving catalyst component A p[S-co-(p,p-C₂₅H₂₃N₃Co)]. The measured Co content was 0.4 wt%.

Application Example 22: Ethylene polymerization

Under oxygen-free and anhydrous conditions, 100 mL of toluene were added to a 200-mL glass reaction bottle, and ethylene gas was fed into the bottle under normal pressure. 3 mL of a toluene solution containing 1M methylaluminumoxane and 0.0187 g of the toluene solution of the catalyst component A p[S-co-(o-C₂₅H₂₅N₃Fe)] prepared in Application Example 18 were added sequentially under stirring, followed by 1 h of reaction carried out at 25°C. An alcohol solution containing 1% hydrochloric acid was used to end the reaction. The obtained polymer was filtered and washed with alcohol three times, followed by drying in vacuo at 40°C for 24 h, giving 1.8 g of polymer. The catalytic efficiency was 9.0×10^5 g PE/molFe·h.

Application Example 23: Ethylene polymerization

Under oxygen-free and anhydrous conditions, 100 mL of hexane were added to a 200-mL glass reaction bottle, and ethylene gas was fed into the bottle under normal pressure. 1 mL of a

toluene solution containing 1M methylaluminoxane and 0.028 g of the toluene suspension of the catalyst component A $p[S\text{-co-(p,p-C}_{25}\text{H}_{23}\text{N}_3\text{Co)}]$ prepared in Application Example 21 were added sequentially under stirring, followed by 1 h of reaction carried out at 40°C. An alcohol solution containing 1% hydrochloric acid was used to end the reaction. The obtained polymer was filtered and washed with alcohol three times, followed by drying in vacuo at 40°C for 24 h, giving 0.8 g of polymer. The catalytic efficiency was 4.0×10^5 g PE/molFe·h.

Application Example 24: Ethylene polymerization

Under oxygen-free and anhydrous conditions, 100 mL of toluene were added to a 200-mL glass reaction bottle, and ethylene gas was fed into the bottle under normal pressure. 5 mL of a toluene solution containing 1M methylaluminoxane and 0.028 g of the toluene suspension of the catalyst component A $p[S\text{-co-(p,p-C}_{25}\text{H}_{23}\text{N}_3\text{Co)}]$ prepared in Application Example 21 were added sequentially under stirring, followed by 1 h of reaction carried out at 50°C. An alcohol solution containing 1% hydrochloric acid was used to end the reaction. The obtained polymer was filtered and washed with alcohol three times, followed by drying in vacuo at 40°C for 24 h, giving 1.2 g of polymer. The catalytic efficiency was 6.0×10^5 g PE/molFe·h.